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SILANE POLYMERS OF DIOLS

by JAMES E. CURRY and JAMES D. BYRD
Propulsion and Vehicle Engineering Laboratory

NASA

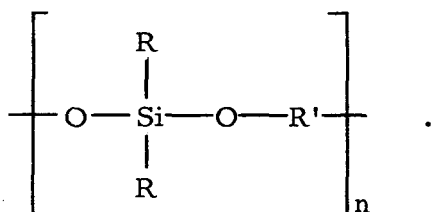
*George C. Marshall
Space Flight Center,
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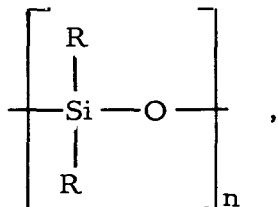
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INTRODUCTION


The need for new materials that will withstand the rigors of the space environment is evident in every phase of spacecraft development. This need is necessitating a sizeable research and development effort in materials science. One of the critical areas is the development of improved non-metallic materials for use as coatings, plastics, adhesives, elastomers, etc. Since most of these materials are composed of complicated long chain molecules known as polymers, a research program for the development of new polymers has been undertaken. This program has led to the development of a number of new types of polymeric materials, but one type, in particular, has shown outstanding properties. These polymers have the general formula,



The silicone polymers having the general formula,



have many outstanding properties although they do have some shortcomings. To improve these properties, the silicone polymer has been modified in a number of ways. The work described here has accomplished these modifications by incorporating the highly stable phenyl

groups, , into the "backbone" of the silicone polymer. This is represented by R' in the first of the above formulae.

ACKNOWLEDGMENT

Appreciation is expressed to Mr. J. K. Davis and Miss Barbara Mrazek for their assistance in the preparation and study of these polymers and to Messrs. Albert C. Krupnick, John W. Barnes, Thomas H. Arnold and Forrest T. Wells, all of the Chemistry Branch, Materials

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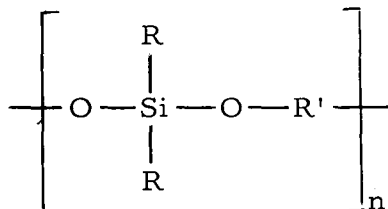
By

James E. Curry
and
James D. Byrd

SUMMARY

In an effort to develop new and improved polymeric materials for space application, a new series of polymers has been prepared. Some of these have shown outstanding thermal stability and good stability when exposed to ultraviolet radiation in a vacuum environment.

High molecular weight polymers of the general type



have been prepared by the reaction of a silyldiamine with various organic diols. Bis (anilino) diphenylsilane has been reacted with such diols as hydroquinone, resorcinol, p,p'-biphenol, 2,7-naphthalenediol, 2,2-propane-bis-(4-hydroxybenzene), 1,6-hexanediol, and 4,4'-dihydroxydiphenyl ether. Of these, the polymer containing the biphenyl linkage, polydiphenylsiloxybiphenyl, has the more desirable properties.

Polydiphenylsiloxybiphenyl is stable to 600°C (1112°F) for short periods of time. Fibers with fairly good tenacity, 0.5 grams per denier, may be drawn directly and continuously from the polymer melt. This polymer forms a hard protective coating on aluminum, remains stable after being heated at 500°C for 60 minutes, and shows no change after 96 hours at 270°C (518°F). It also forms good transparent semiflexible films and has good tensile strength as an ambient temperature adhesive.

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MATERIALS DIVISION
PROPULSION AND VEHICLE ENGINEERING LABORATORY

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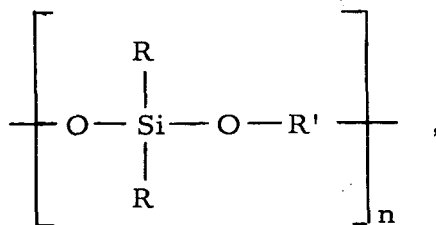
James D. Byrd

ABSTRACT

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The purpose of this study was to synthesize and develop a new class of polymers which have improved physical and chemical properties.

Polymers which have useful properties and very good thermal stability were prepared by combining the thermally stable aromatic rings with the silicon polymer chain. These polymers have the general structure,



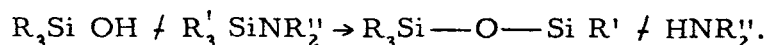
where R represents an alkyl or aryl group and R' is an alkyl, aryl substituted alkyl, biphenyl or diphenyl ether linkage.

The polymer showing the best properties is polydiphenylsiloxo-biphenyl which is stable to 600°C (1112°F) for short periods of time. It is also reasonably stable when exposed to ultraviolet radiation, has good fiber and film forming properties, and is a good adhesive at ambient temperatures.

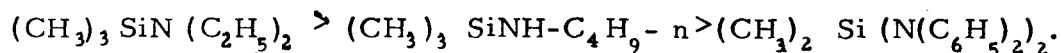
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Thermogravimetric analysis of this polymer showed a weight loss of 18% at 500°C and 46% at 900°C.

The cleavage of Si - N bonds by nucleophilic reagents is discussed in numerous reports in the literature (Ref. 3, 4, 5, 6, and 7). Pike (Ref. 8 and 9) has studied the rate of condensation of monofunctional silylamines with monofunctional silanols,



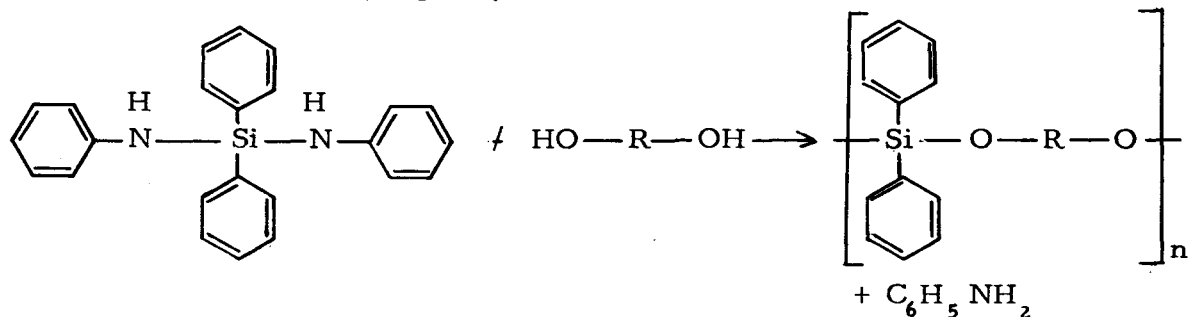
The extent and rate of reaction are dependent upon the steric hindrance around both the silicon-nitrogen bond and the hydroxyl group of the alcohol and acidity of the attacking alcohol. The rate of reaction of silylamines toward a given silanediol decreased in order,



However, our work has shown that the stable silylamine, bis (anilino) - diphenylsilane, $(C_6H_5)_2 Si (NHC_6H_5)_2$, will react with a number of dihydroxy compounds at rates which are adequate to produce high molecular weights in relatively short periods of time. This silylamine appears to have enough steric hindrance so that there is no apparent tendency to cyclize.

EXPERIMENTAL

Our investigation encompassed the melt polymerization of organic diols with bis-(anilino) diphenylsilane.

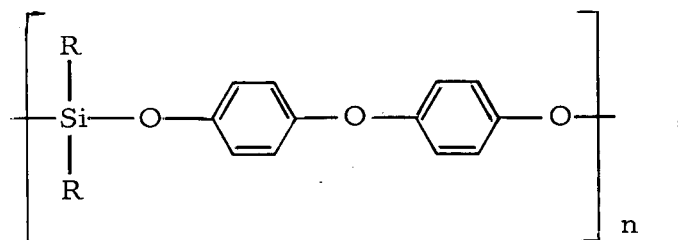


This included such diols as hydroquinone, resorcinol, p, p'-biphenol, 2, 7-naphthalenediol, 2, 2-propane-bis-(4-hydroxybenzene) -(Bisphenol A), 1, 6-hexanediol, and 4, 4'-dihydroxy-diphenyl ether. Alkylaryl

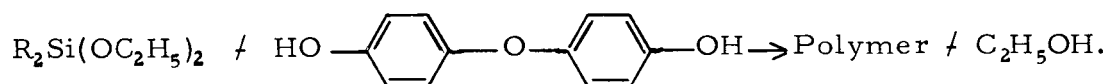
Division for their assistance in the analysis and characterization of these materials. Appreciation also is expressed to Dr. Robert E. Burks of Southern Research Institute for his assistance in this study.

STATE OF THE ART

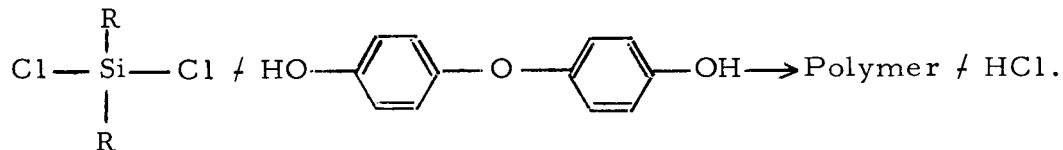
MacFarland and Yankura (Ref. 1) reported the preparation of a polymer with the structure,



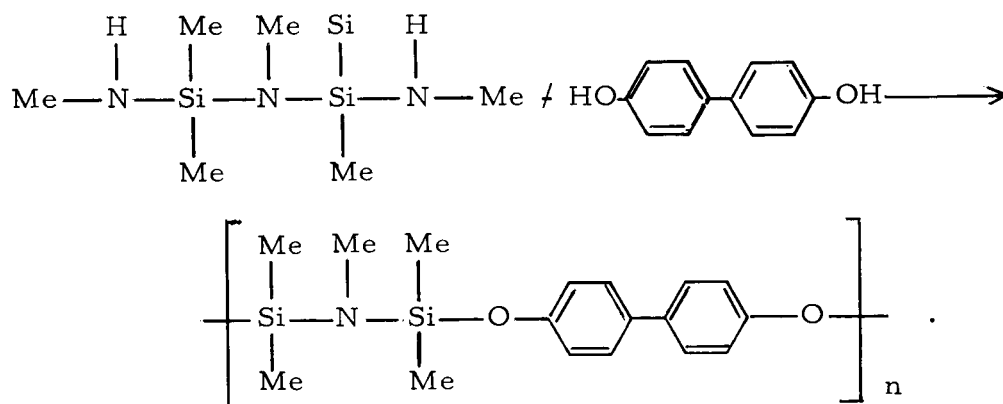
which can be prepared by two different methods. One method of preparation was by the following alcoholysis type condensation reaction:



The other was a condensation between the chlorosilane and the dihydroxydiphenylethers.



Breed and Elliott (Ref. 2) have reported a polymer with good thermal stability which was prepared by the following reaction:



copolymer was prepared also. All of these polymers showed elasticity at elevated temperatures, and fibers could be drawn from the elastic melt.

Monomers

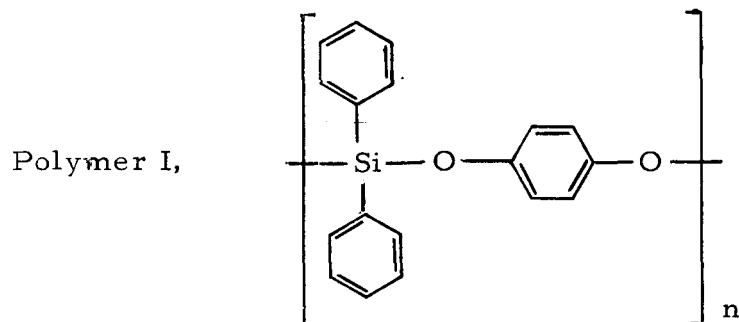
Bis(anilino) diphenyl silane was prepared using the procedure of Anderson (Ref., 3) by the reaction of diphenyldichlorosilane and aniline. Three hundred and twelve ml (4.0 moles) of freshly distilled aniline and 400 ml of benzene were placed in a round bottom flask. Two hundred and eight ml (1.0 moles) diphenyldichlorosilane in 250 ml of benzene were added dropwise with rapid stirring. After refluxing for one hour, the reaction products were allowed to stand overnight and then were filtered. The filter cake was slurred in 2.5 liters of boiling benzene, and the aniline hydrochloride was removed by filtrations. The filtrate was evaporated to approximately one half of its volume to effect crystallization of the desired monomer. The bis(anilino) diphenylsilane was dried at room temperature under reduced pressure. The final product was a white crystalline material that melted at 156-161°C. The calculated values for the elemental analysis of this compound are C, 78.69%; H, 6.01%, N, 7.65%; Si, 7.65%, and values found were C, 78.00%; H, 5.73%; N, 7.20%, Si, 8.00%.

The organic diols were obtained from commercial sources, but in each case they were recrystallized before using. The Bisphenol-A was obtained from Dow Chemical, and all other diols were obtained from Eastman Organic Chemicals.

Polycondensations

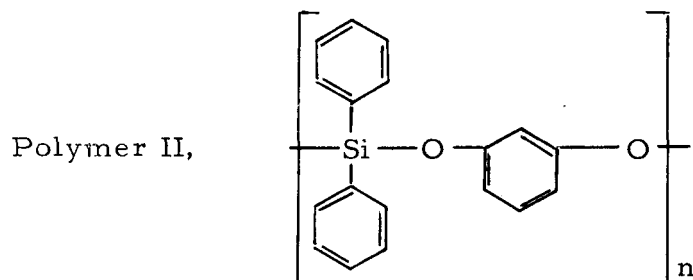
Equimolar amounts of the monomers were placed in a thick-walled resin kettle which was equipped with liquid take-off condenser and a vacuum source. The kettle was heated, and the contents were stirred with a hot plate-magnetic stirrer combination. A heating mantle was used on the kettle to help remove the amine as it was evolved. The monomers were first mixed in the solid state, and then heat was applied slowly. The monomers were thoroughly mixed after they melted. After about 30 minutes, vacuum was applied slowly. The final reaction conditions were about 1 mm Hg vacuum at about 300-325°C. The heating time was generally six hours.

Polymers prepared by the above reaction are as follows:



M. P. above 300°C

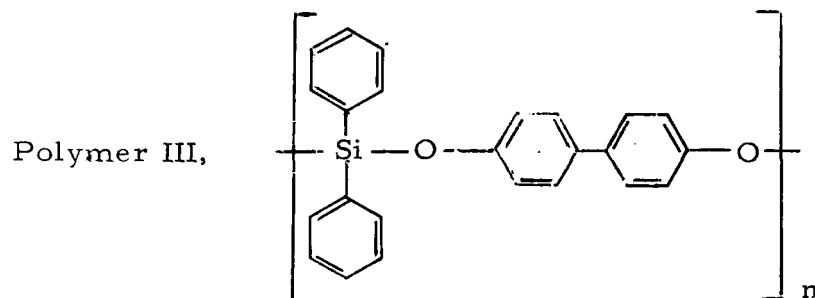
Analytical: Calculated for $(C_{18}H_{14}O_2Si)_n$: C, 74.45%; H, 4.86%; Si, 9.67%.
 Found-- C, 73.43%; H, 4.54%; Si, 10.49%.



A yield of 96.7% of theory of a hard, brittle polymer was obtained.

M. P. 253-257°C

Analytical: Calculated for $(C_{18}H_{14}O_2Si)_n$: C, 74.45%; H, 4.86%; Si, 9.67%.
 Found-- C, 74.45%; H, 4.86%; Si, 10.56%.

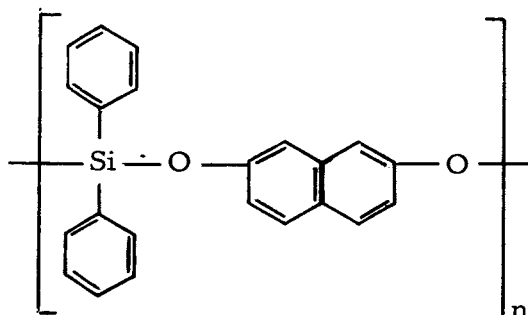


A yield of 98.4% of theory of a tough, semiflexible polymer was obtained.

M. P. above 300°C

Analytical: Calculated for $(C_{24}H_{18}O_2Si)_n$: C, 78.65%; H, 4.95%; Si, 7.66%.
 Found-- C, 78.13%; H, 4.94%; Si, 8.7%.

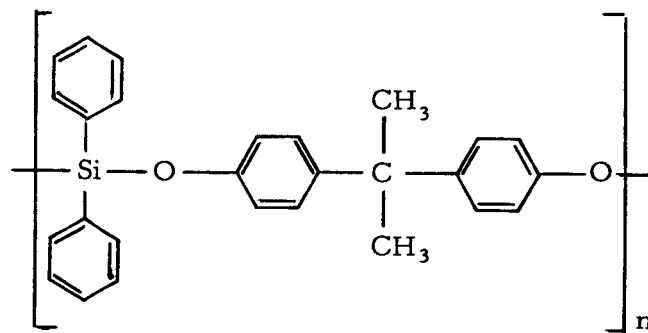
Polymer IV,



M. P. 123-125°C

Analytical: Calculated for $(C_{22}H_{16}O_2Si)_n$: C, 77.75%; H, 4.71%; Si, 8.20%.
 Found-- C, 77.67%; H, 4.74%; Si, 8.92%.

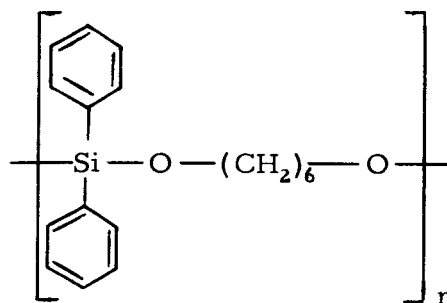
Polymer V,



M. P. 99-100°C

Analytical: Calculated for $(C_{27}, O_2, Si)_n$: C, 79.37%; H, 5.92%; Si, 6.88%.
 Found-- C, 78.41%; H, 5.94%; Si, 7.10%.

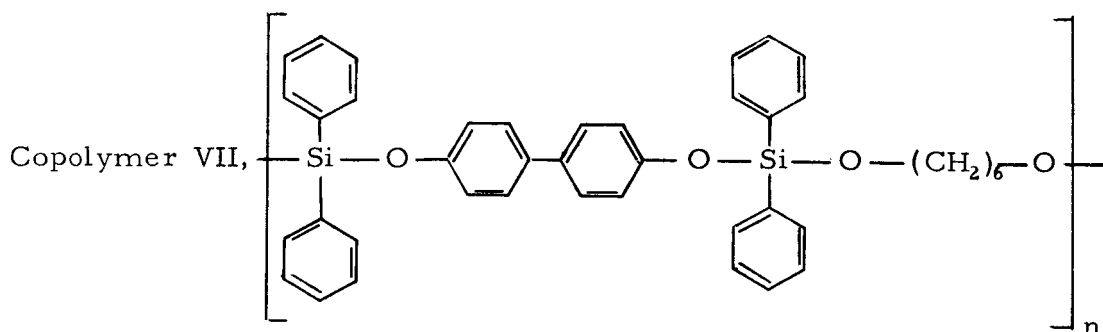
Polymer VI,



A yield of 96.0% of theory of a sticky solid polymer was obtained.

M. P. 253-257°C

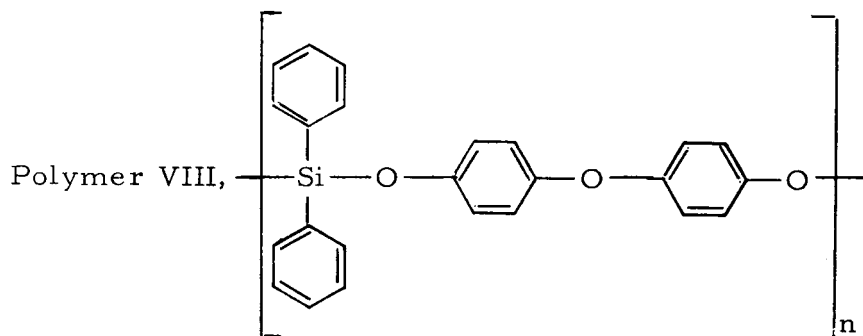
Analytical: Calculated for $(C_{18}H_{22}O_2Si)_n$: C, 72.44%; H, 7.43%; Si, 9.41%.
 Found-- C, 71.13%; H, 7.11%; Si, 9.86%.



A very tough semi-flexible polymer was formed.

M. P. above 300°C

Analytical: Calculated for $(C_{21}H_{28}O Si)_n$: C, 75.86%; H, 6.06%; Si, 8.45%.
 Found-- C, 74.78%; H, 5.08%; Si, 10.7%.



M. P. 127-130°C

Analytical: Calculated for $(C_{24}H_{18}O_3 Si)_n$: C, 75.33%; H, 4.74%; Si, 7.34%.
 Found -- C, 75.46%; H, 4.67%; Si, 7.96%.

The properties of the polymers prepared are given in Tables I and II.

The infrared spectra obtained on the polymers presented in this report have been studied, and the correlation of data from these related compounds gives credence to their assigned structures (FIG 1, 2, 3, and 4). It is possible to give assignments to aromatic substitution patterns, hydrocarbon groups, and silicon-to-oxygen bonds, etc. In polymers I, III, V, VII, and VIII, there is a common adsorption band between 824 and 835 wave numbers (cm^{-1}). This band can be attributed to the C-H out-of-plane deformation by the 1,4 disubstituted aromatic rings. In addition, all of the polymer spectra show two distinct adsorption bands at 720 and 690 cm^{-1} . These adsorption bands arise from the mono-substituted aromatic rings attached to the silicon. In the case of polymers II and IV, identification of the aromatic structures, other than the mono-substituted system, is difficult. It may be possible that the very strong adsorption bands at 768 cm^{-1} in polymer II are caused by the three adjacent hydrogen atoms in the 1, 3 disubstituted aromatic ring. Polymer IV does not show any specific bands in the 900 to 650 cm^{-1} region that would enable one to assign aromatic substitution. However, the shifting of the 1600 and 1590 cm^{-1} may be an indication of the naphthalene structure. Therefore, additional data on similar polymer structures would be required before positive assignments can be made.

Based on the correlation of data from these polymers and other organo-silicon structures, the sharp medium adsorption bands at 1429 cm^{-1} and the strong broad system at 1125 cm^{-1} can be attributed to the Si-Phenyl linkage. The Si-O linkage gives rise to rather broad band system observed just below 1100 cm^{-1} . The adsorption band observed between 1200 to 1300 wave numbers is apparently due to the phenoxysilicon portion of these polymer structures. This phenoxy-silicon assignment is indicated by the appearance of the very strong band in all of the spectra, except in the case of polymer VI where this structure does not occur. The structural arrangement of the propyl group in polymer V should give rise to a vibrational pattern similar to that of an isopropyl radical. This pattern is confirmed by the strong peak at 1429 cm^{-1} and the two weak peaks at 1385 and 1363 cm^{-1} .

Polymer VII is a co-polymer of the structures suggested for polymers III and VI. It is evident when comparing the spectra of III and VII that there is little difference between these spectra to suggest a new structure with the exception of the weak aliphatic CH doublet between 2850 and 2940 wave numbers. Thus, the infrared spectra of the polymer VII does not indicate whether the suggested structure is correct. At this time, it is

not understood why the adsorption intensity of this CH doublet between 2850 and 2940 cm^{-1} is weak, nor does the structure for polymer VII suggest why the normal aliphatic stretching mode should be attenuated to the degree observed in the spectrum. Correlation assignments for the diphenoxy linkage in polymer VIII could not be made from the infrared spectra.

The N-H vibration band of amino-silanes between 3320 and 3340 cm^{-1} is absent in each case, indicating that there is no bis (anilino) diphenyl silane present.

DISCUSSION

With the exception of polymer VI, all products are soluble in tetrahydrofuran (THF), dimethylformamide (DMF) or dimethylsulfoxide (DMSO). Protective coatings from THF solutions upon ceramic-coated metal plates have improved ultraviolet stability. (See Table IV.) The change in percent reflectance with wave length for irradiation time of 48 hours at a pressure of 2×10^{-5} mm Hg was determined.

The thermal stabilities of all the polymers are given in FIG 5, 6, and 7. These were obtained by thermogravimetric analysis (TGA) in a nitrogen atmosphere by using a heating rate of 4.1°C per minute.

FIG 5 presents the TGA data of the four polymers which are true aromatic types. It may be observed from these data that polymer III has the best thermal stability, losing 10% of its weight at 600°C. FIG 6 shows the effect of using a propyl group or oxygen between the two phenyl groups in this polymer. Again, polymer III is the most stable. FIG 7 shows the relative stabilities of aromatic versus aliphatic "chain units" and a copolymer which contains both. It may be seen that the aliphatic polymer lost most of its weight at 500°C while a 50/50 copolymer is only slightly less stable than the totally aromatic polymer.

When polymer III was prepared with starting materials which had been recrystallized three times, fairly strong fibers could be drawn continuously from its melt. These fibers showed an initial tenacity of 0.5 grams/denier. Since they may be hot or cold drawn, their strength should be greatly increased if proper spinning methods are used. Brittle fibers could be drawn from the melt of all other polymers. Polymer VIII gave a semi-flexible, fairly weak fiber which showed improved strength after drawing over a hot plate.

A thermally pressed film of 15 mil thickness of polymer III had a tensile strength of 3560 psi with an 11% elongation. When tested as a hot melt adhesive on 1020 mild steel, the average tensile shear strength of the polymer was 3920 pounds per square inch.

Polymer I formed a good hot melt adhesive and had tensile shear strength of 2950 psi. When the shear tensile strength of polymers I and III was compared, an increase of about 33% was observed due to the replacement of a benzene ring by diphenyl.

The thermal stability of copolymer VII was considerably better than the polymer (VI) containing exclusively alkyl "chain units" and was only slightly inferior to the structure having only diphenyl group (III). Unfortunately, polymer VII could not be tested as a hot melt adhesive because of insufficient melting at 400°C (725°F). Number average molecular weights ranging up to 180,000 have been obtained with polymer III. Table III shows the range of molecular weights obtained in various reactions. No attempts were made to define conditions for obtaining maximum or optimum molecular weights. However, it may be noted in Table III that reaction time affects molecular weights.

Polymer III produces a flexible coating on aluminum which may be cured by heating at 270°C (518°F) for 16 hours. This film remained stable after being heated to 400°C (752°F) for four hours and showed no decomposition after 96 hours at 270°C (518°F).

CONCLUSIONS

This investigation has led to the discovery and initial development of a new polymer system which gives many indications of being superior to presently available materials. One of the most outstanding properties is its stability at elevated temperatures, being stable at 500°-600°C (932°-1112°F) for short periods of time.

The best of these polymers appear to be suitable for improved coatings, laminates, films, fibers, molding compounds, and adhesives. In each of these applications, the materials have shown properties which suggest their potential commercial application. The use of these materials as thermal control coatings, as molding compounds, and as adhesives may be of value in several areas of launch vehicle technology.

The application of these polymers as thermal control coatings appears to be especially promising. A thin coating on aluminum remained stable after four hours at 400°C (752°F). This coating also showed good stability when exposed to ultraviolet irradiation as compared to a commercial high temperature silicone coating.

FUTURE PLANS

Since the initial results of this investigation appear quite favorable, we presently plan to evaluate these materials in more detail. Plans are being made to evaluate further the fiber-forming properties of polymer III and its use as a compression molding compound. A program also is planned to develop a chemical cure for this polymer so that its use as an adhesive might be improved.

Model compounds of the polymeric units will be prepared in order to study their chemical stability and reactivity.

Since these materials have shown promise as high temperature coatings, they are being evaluated further and compared with other new high temperature polymer systems.

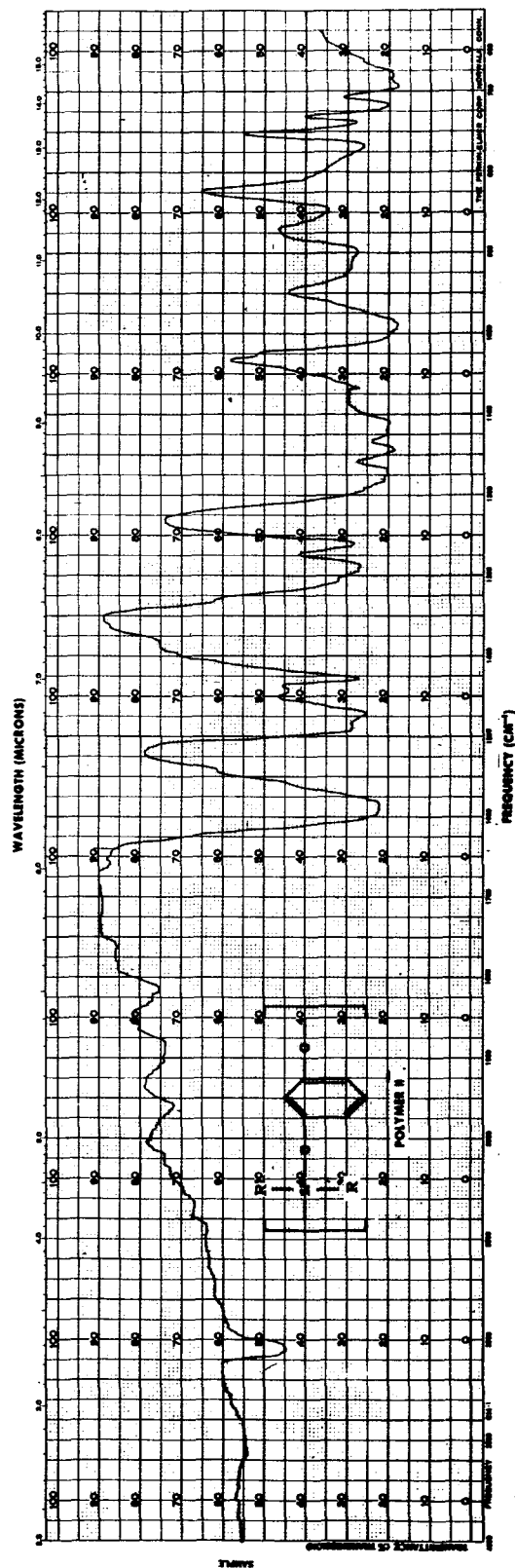
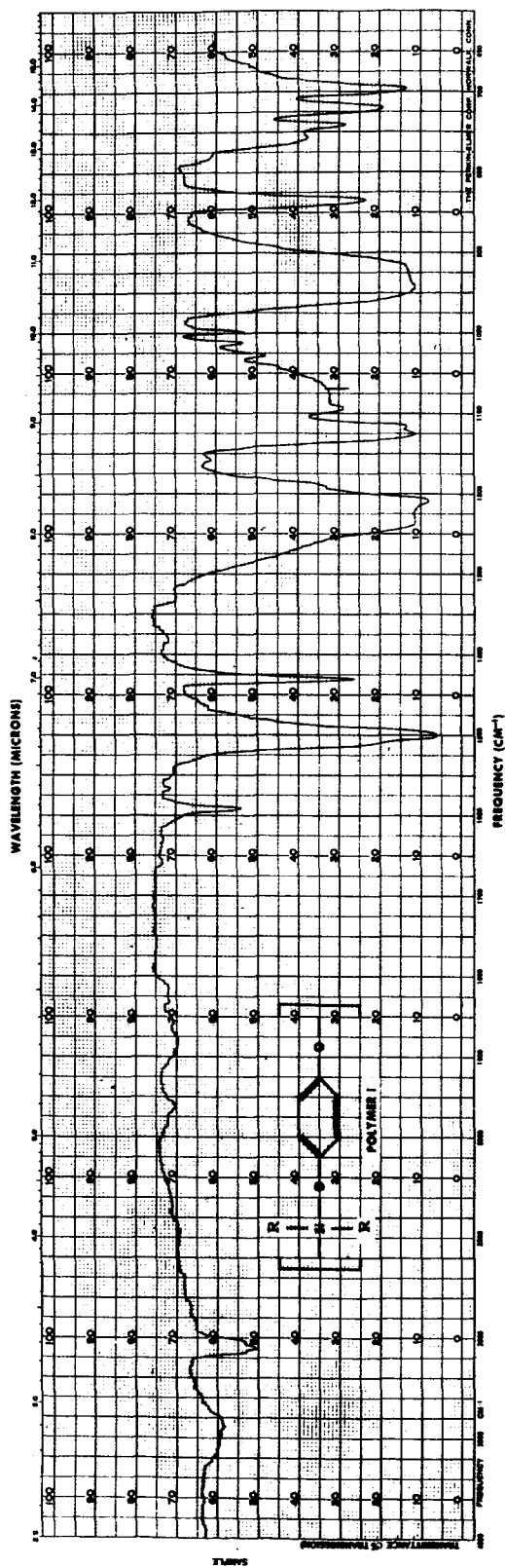
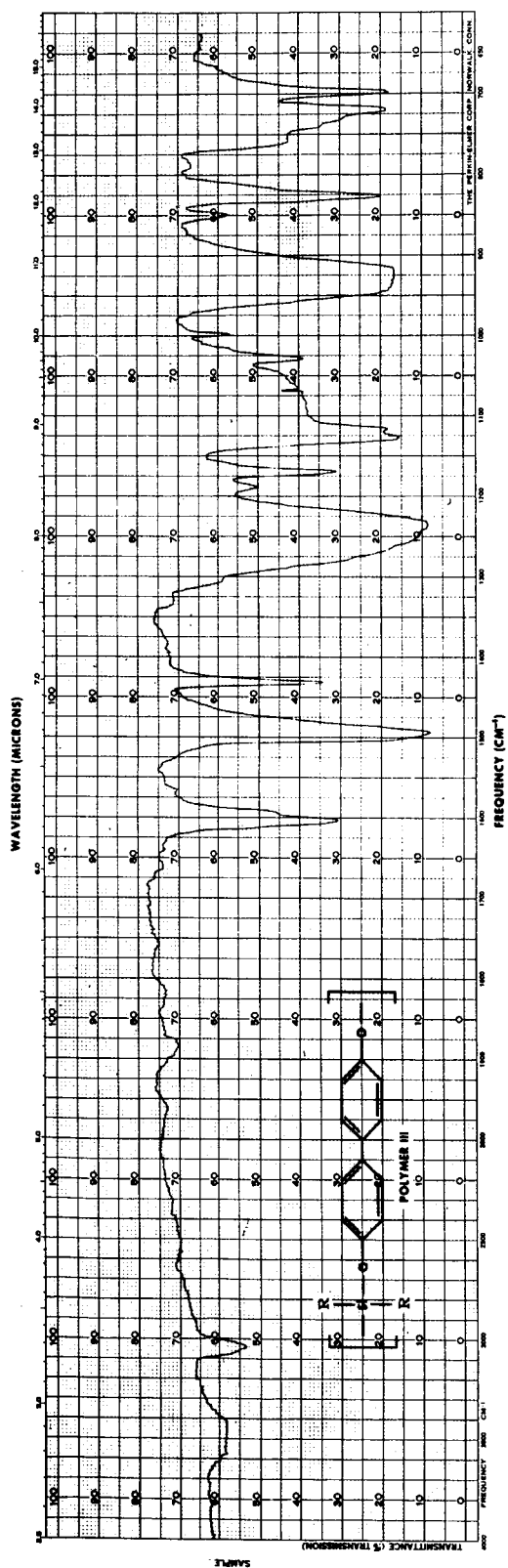


FIGURE 1. INFRARED SPECTRA



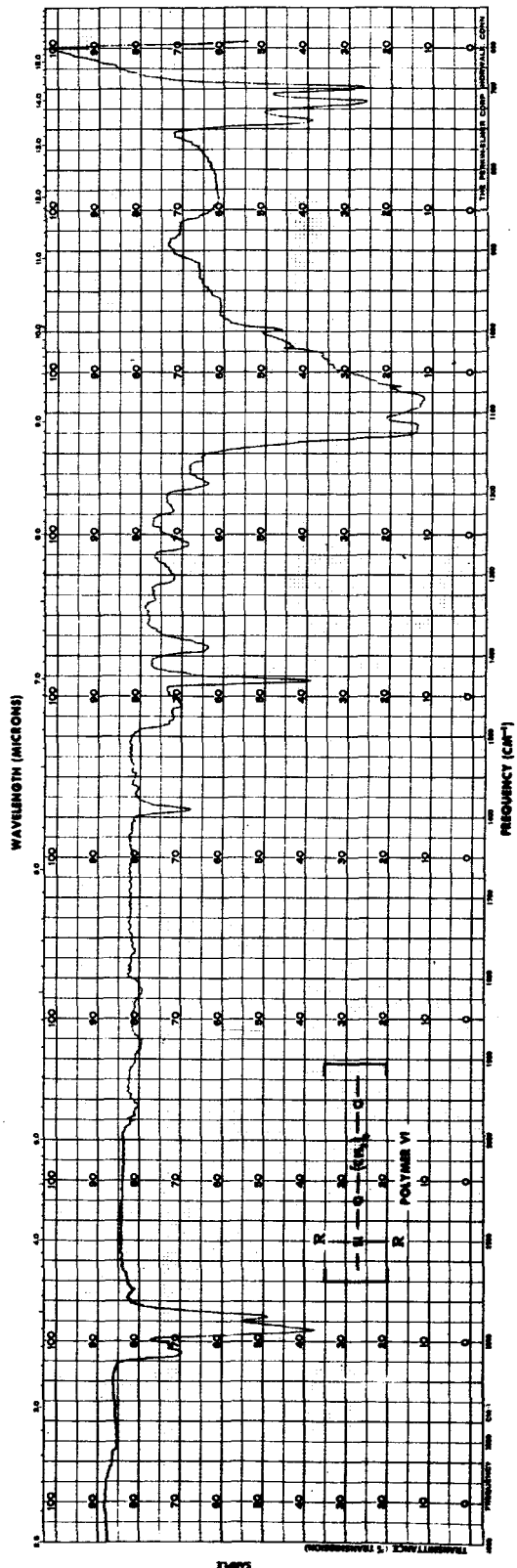
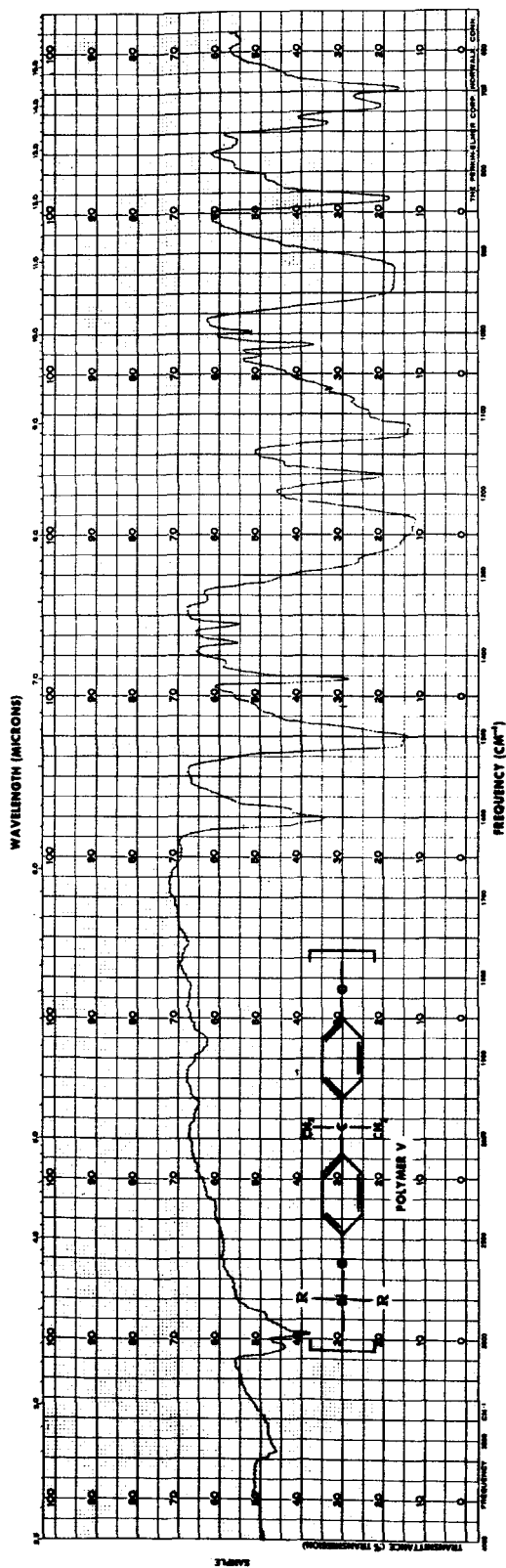


FIGURE 3. INFRARED SPECTRA

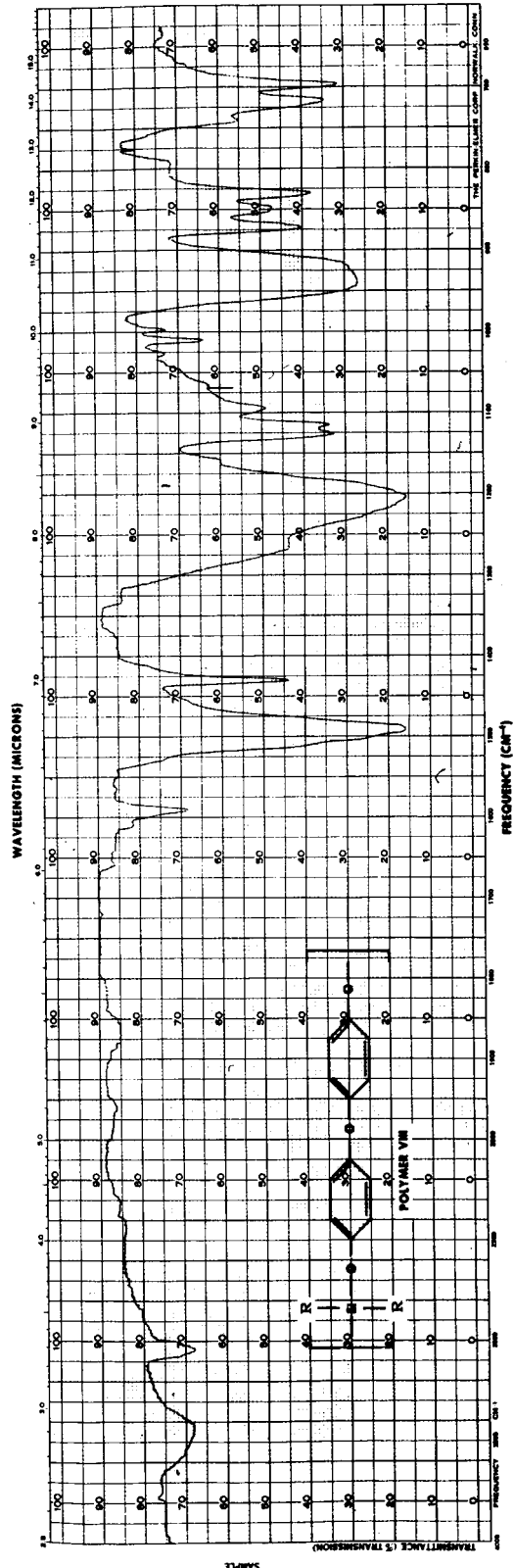
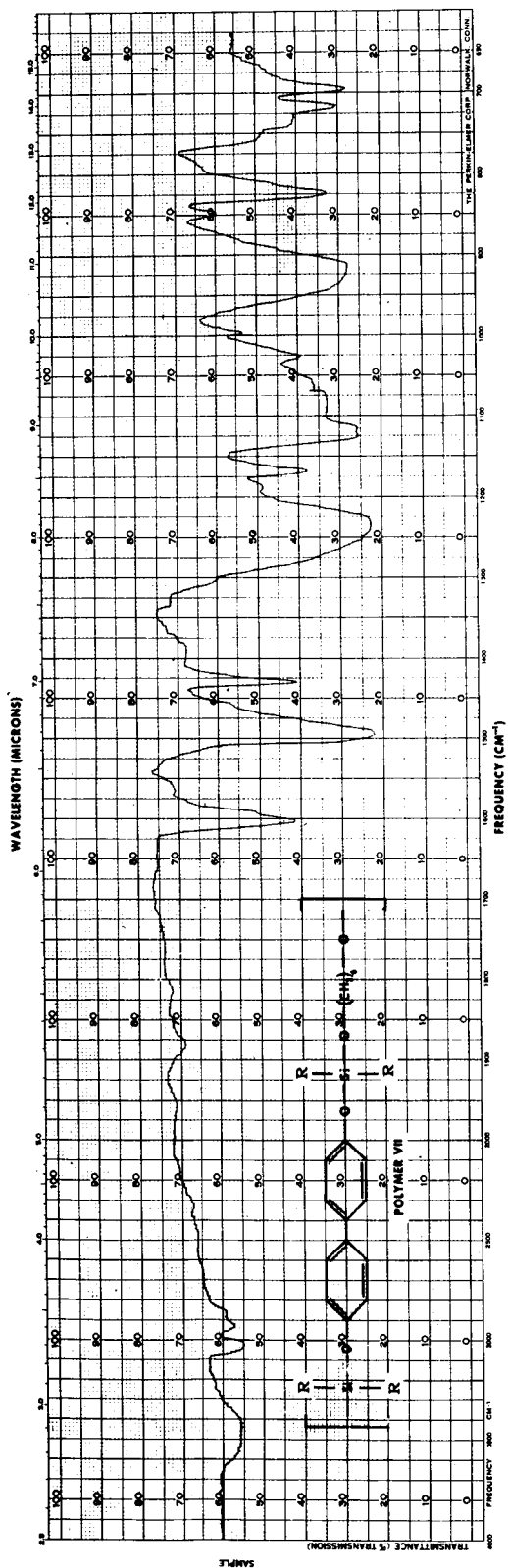
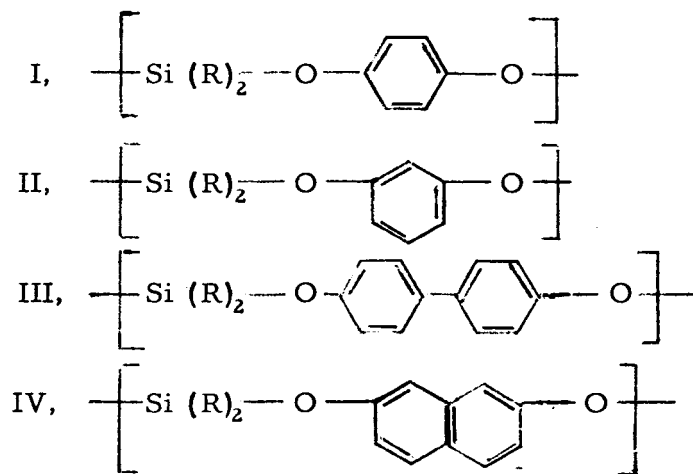
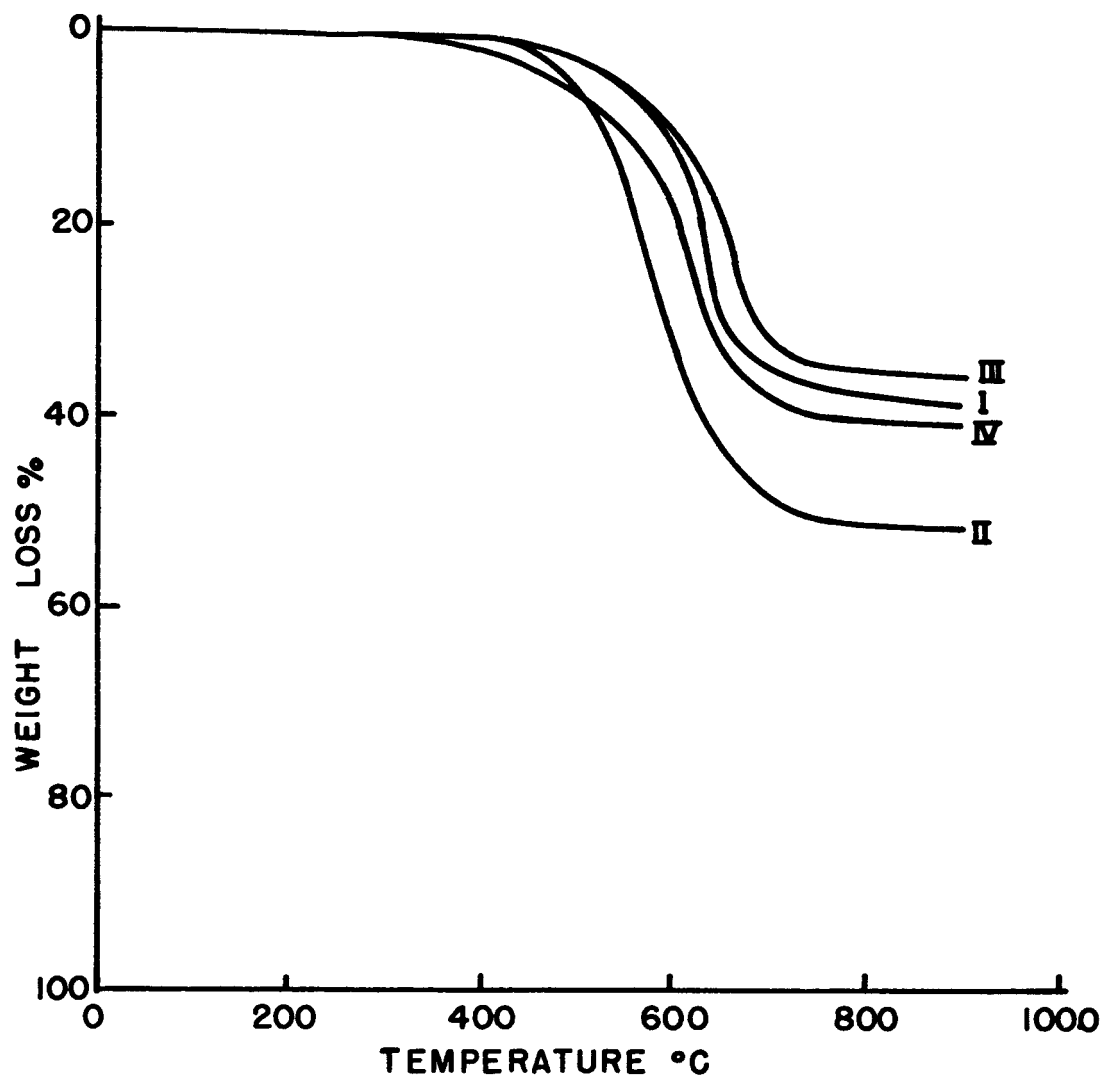
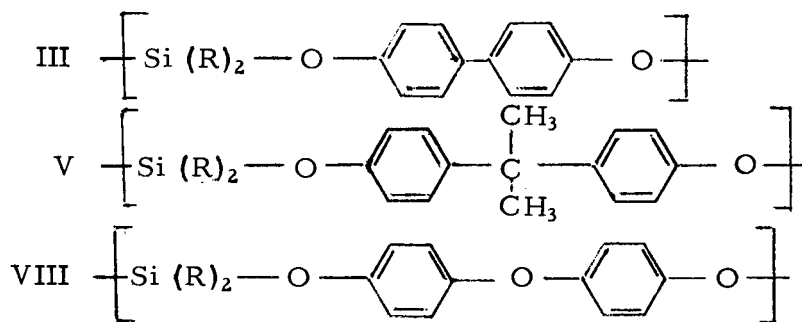
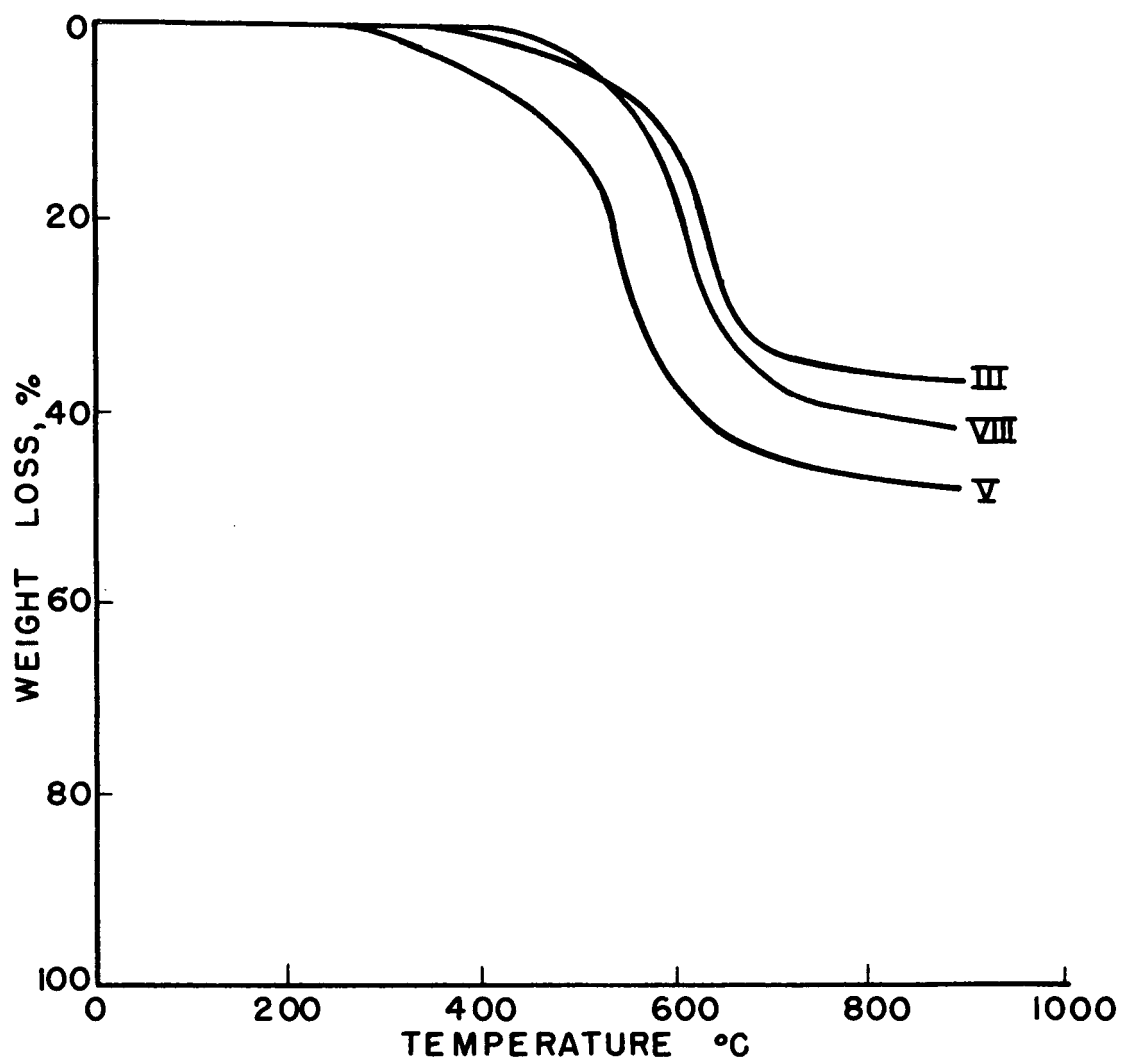


FIGURE 4. INFRARED SPECTRA



R represents a phenyl_group

FIGURE 5. THERMOGRAVIMETRIC ANALYSIS OF POLYMERS



R represents a phenyl group

FIGURE 6. THERMOGRAVIMETRIC ANALYSIS OF POLYMERS

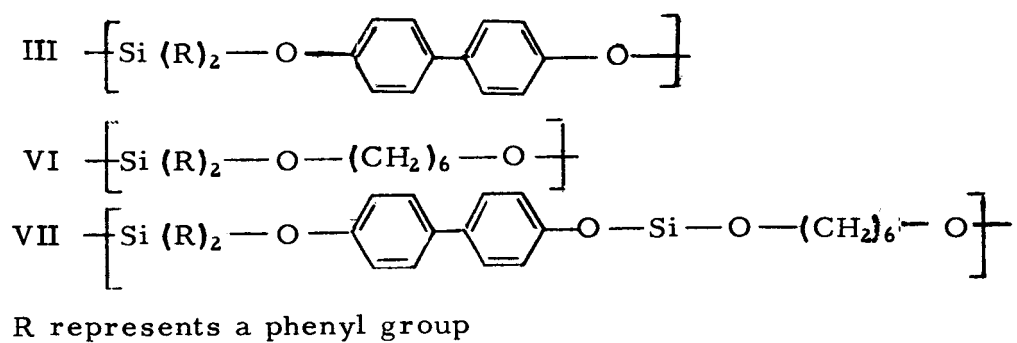
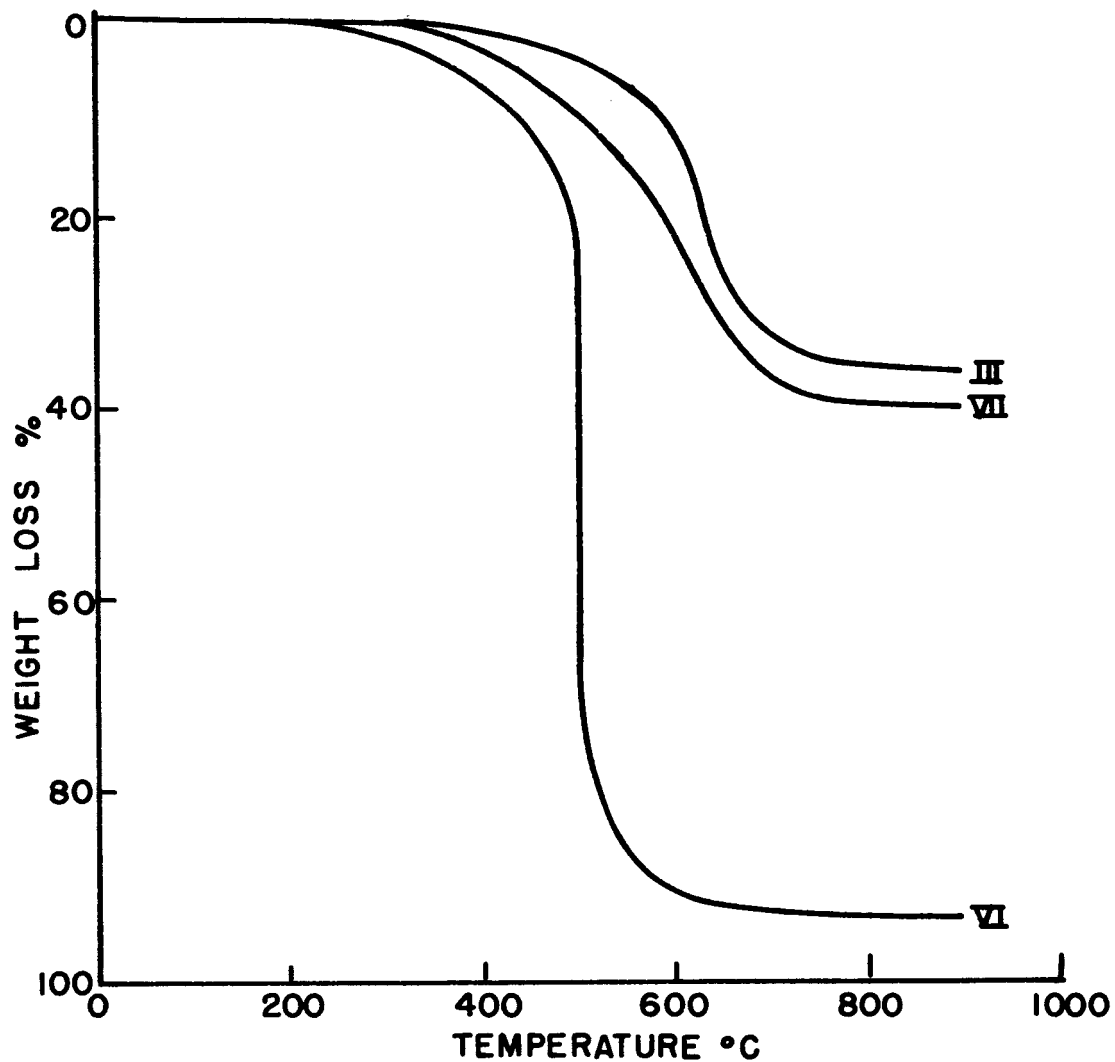
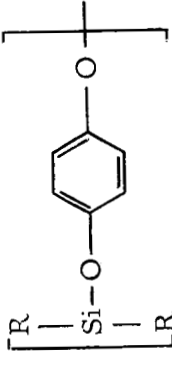
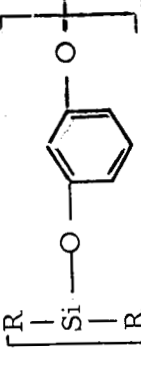
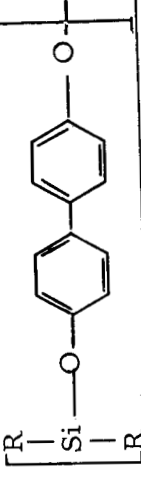
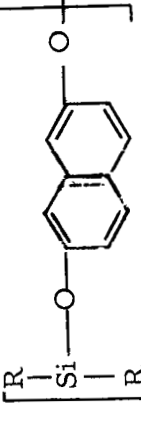
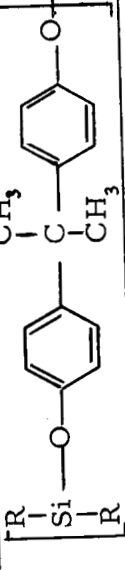


FIGURE 7. THERMOGRAVIMETRIC ANALYSIS OF POLYMERS

TABLE I. SILICON POLYMERS OF ARYL DIOLS

| Polymer Repeating Unit | Description of Polymer | Melting Point° C |
|--|--|------------------|
|  I | Hard, slightly brittle, amber, solid | above 300 |
|  II | Hard, slightly brittle, amber, solid | 240-245 |
|  III | Hard, tough, semi-flexible, light amber, solid | above 300 |
|  IV | Hard, brittle, dark brown, solid | 123-125 |
|  V | Hard, brittle, amber, solid | 99-100 |

All polymers were soluble in DMF, THF, and DMSO.

R represents a phenyl group.

TABLE II. SILICON POLYMERS OF ALKYL DIOLS, ALKYL-ARYL DIOLS AND DIHYDROXYPHENYLETHER

| Polymer Repeating Unit | Description of Polymer | Melting Point° C |
|---|--|---------------------|
| $\left[\begin{array}{c} \text{R} \\ \\ \text{Si} - \text{O} - (\text{CH}_2)_6 - \text{O} \\ \\ \text{R} \end{array} \right]$ | Light, amber, soft, tacky gum | 253-257 |
| $\left[\begin{array}{c} \text{R} \\ \\ \text{Si} - \text{O} - \text{O} - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - \text{O} - \text{Si} - \text{O} - (\text{CH}_2)_6 - \text{O} \\ \qquad \\ \text{R} \qquad \text{R} \end{array} \right]$ | Hard, tough, semi- flexible, light amber, solid | above 300 |
| $\left[\begin{array}{c} \text{R} \\ \\ \text{Si} - \text{O} - \text{O} - \text{C}_6\text{H}_4 - \text{O} - \text{C}_6\text{H}_4 - \text{O} \\ \qquad \\ \text{R} \qquad \text{R} \end{array} \right]$ | Hard, tough, semi- flexible, fiber-forming polymer | 127-130 |

All polymers with the exception of VII were soluble in DMF, THF, and DMSO.

R represents a phenyl group.

TABLE III. MOLECULAR WEIGHTS OF POLYMER NO. III

| Experiment Number | Time of Reaction | M. W. (a) | Physical Description | | M. P. °C | Film-Forming (b) quality |
|----------------------|---------------------|--------------|----------------------|---------------|----------|--------------------------------|
| | | | Color | Flexibility | | |
| 1 | 3 | 38,000 | Light Gray | Brittle | 135-137 | None |
| 2 | 6 | 75,000 | Light Amber | Semi-flexible | 300 | Good |
| 3 | 6 | 180,000 | Light Amber | Semi-flexible | 300 | Fair (c) |

(a) Determined by light scattering technique by Southern Research Institute, Birmingham, Alabama.

(b) Thermally pressed film.

(c) Sample of M. W. 180,000 did not melt sufficiently to form uniform film.

TABLE IV. ULTRAVIOLET IRRADIATION

| Irradiation Time: 48 Hours | | | | | |
|--|----------------------|--------------|------------------------------------|--------------|--|
| Pressure: 2.0×10^{-5} mm Hg | | | | | |
| U. V. Source: Hanovia Quartz Mercury-Vapor | | | | | |
| Lamp, Type 54A-10 | | | | | |
| <u>Polymer III</u> | | | <u>Control Sample</u> ¹ | | |
| <u>Wave length</u> | <u>% Reflectance</u> | | <u>% Reflectance</u> | | |
| <u>mμ</u> | <u>Initial</u> | <u>Final</u> | <u>Initial</u> | <u>Final</u> | |
| 400 | 69.0 | 42.5 | 64.0 | 25.0 | |
| 425 | 79.0 | 53.0 | 78.5 | 35.0 | |
| 450 | 82.0 | 60.5 | 81.5 | 46.0 | |
| 475 | 84.0 | 68.0 | 84.5 | 57.0 | |
| 500 | 85.0 | 72.5 | 85.5 | 65.0 | |
| 525 | 87.0 | 76.0 | 87.5 | 72.0 | |
| 550 | 87.0 | 78.0 | 87.0 | 76.5 | |
| 575 | 87.0 | 78.5 | 87.5 | 79.0 | |
| 600 | 85.0 | 79.0 | 87.0 | 81.0 | |
| 625 | 85.0 | 81.0 | 85.0 | 82.0 | |
| 650 | 85.0 | 81.5 | 85.5 | 82.5 | |
| 675 | 85.0 | 81.5 | 85.5 | 82.0 | |
| 700 | 85.0 | 82.0 | 85.0 | 82.0 | |

¹ A commercial high temperature coating material (Dow Corning 808)

REFERENCES

1. MacFarland, R., and Yankura, E. S., "Synthesis of Regulated Structure Polyphenylether - Siloxane Block Copolymers, " Contract No. DA-19-020-ORD-5507, Quarterly Report No. 7, Naugatuck Division of United States Rubber Company.
2. Breed, L. W., and Elliott, R. L., "Synthesis of Elastomers Containing Si-N Bonds in the Main Chain, " Contract #DA-23-072-ORD-1687, Quarterly Report No. 5, Midwest Research Institute.
3. Rochow, E. G., Chemistry of the Silicones, John Wiley and Sons, New York, New York, 2nd ed., 1951, P. 58.
4. Larsson, E., and Majorne, R., Acta. Chemica Scandinavica, 5, 964 (1951).
5. Speir, J. L., Journal of the American Chemical Society, 74, 1003 (1952).
6. Langer, S. H., Connell, S., and Wender, I., Journal of Organic Chemistry, 23, 50 (1958).
7. Smith, B., Svensk Kemisk Tidskrift, 65, (1953); Chemical Abstracts, 48, 9907 g. (1954).
8. Pike, R. M., Journal of Organic Chemistry, 26, 232 (1961).
9. Pike, R. M., Journal of Polymer Science, 50, 151 (1961).
10. Anderson, H. H., Journal of the American Chemical Society, 73, 5802 (1951).

SILANE POLYMERS OF DIOLS

By

James E. Curry
and
James D. Byrd

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R. E. SHANNON

Chief, Non-Metallic Materials Branch



W. R. LUCAS

Chief, Materials Division



F. B. CLINE

Acting Director, Propulsion and Vehicle Engineering Laboratory

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